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GEOLOGICAL SURVEY

CHEMICAL CHARACTERISTICS FOR 23
WESTERN WASHINGTON RIVERS, 1961-80

By

David P. Dethier

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This report is preliminary and has not been reviewed for conformity with U.S. Geological Survey editorial standards and stratigraphic nomenclature. Any use of trade names is for descriptive purposes only and does not imply endorsement by the USGS.

Seattle Washington
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INTRODUCTION

Western Washington is characterized by moderate to high annual precipitation and abundant, chemically dilute surface waters. Most of the major cities and many industries in the area use surface-water supplies. With the exception of chlorination for drinking-water supplies, chemical treatment is generally not required for these high-quality waters. However, as the urban areas of western Washington continue to expand, significant degradation of water quality has occurred (Welch, 1968) and protection of surface waters from point and nonpoint sources of pollution has increasingly concerned Federal and State agencies, municipal water departments, water districts, and other planners and individuals interested in water quality.

In order to accurately predict the effects of strategies to protect or restore water quality, such as a municipal-waste diversion or regional efforts to reduce rainfall acidity (Federal Interagency Work Group, 1978), present surface-water quality must be known. A precise knowledge of surface-water chemistry and elemental transport also aids in answering more basic questions about geochemical, geomorphic, and hydrologic processes and their effect on water quality.

Although water-quality relationships have been reported for individual rivers (for instance, Santos and Stoner, 1974) and drainage basins in western Washington (Drost and Lombard, 1978), there are no published reports that summarize regional water-quality relationships. Yet these data are vital for studies of the importance of point and nonpoint sources of pollution, and investigations of long-term trends in water quality (for instance, see Smith, Hirsch, and Slack, 1981; Slack and others, 1981).

This study summarized chemical data and the relationship between discharge and the major, dissolved inorganic constituents for 23 selected rivers in western Washington, for the period 1961-80. Discharge/concentration relations, summary statistics, and evaluations of the amounts and proportions of major anions and cations provide a good characterization of the average chemical composition of rivers, its variability and extreme values, and relationship to basin geology. The study provides a data base for comprehensive investigations of river geochemistry, and geomorphic topics like the rate of chemical denudation. However, those topics lie outside the scope of this study, and are mentioned only briefly.

ACKNOWLEDGMENTS

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SETTING

Location, Climate, and Vegetation

The rivers used in this study are located in western Washington, and drain five major geologic provinces (fig. 1). The largest cities lie in the Puget Sound area. The urban complex which stretches from Everett to Tacoma contains about 60 percent of Washington's population. Drainage basins, with the exception of the North Fork Quinault River, are at least partially developed upstream from each sample site. Parts of basins that lie in the Puget Sound area are heavily developed and contain numerous potential nonpoint sources of pollution. In contrast, river basins that drain the Olympic Mountains province are mostly undeveloped.

Regional climate is cool, moist maritime, and is characterized by cool, wet winters, and warm, drier summers. Mean annual precipitation ranges from about 500 to 4500 millimeters (fig. 2); the highest precipitation is found in the Olympic Mountains and the Cascade Range, and the lowest amounts are reported in the Puget lowland, in the "rain shadow" of the Olympic Mountains. In most parts of western Washington, 70 to 80 percent of the annual precipitation falls between October and May; most moisture falls as snow above an elevation of about 900 m. Runoff in most rivers is highest in early winter and during the spring snowmelt season, and annual peak flows most commonly occur during these periods. Although flows typically are lowest between July and early October, discharge during the summer months remains significant in many drainage

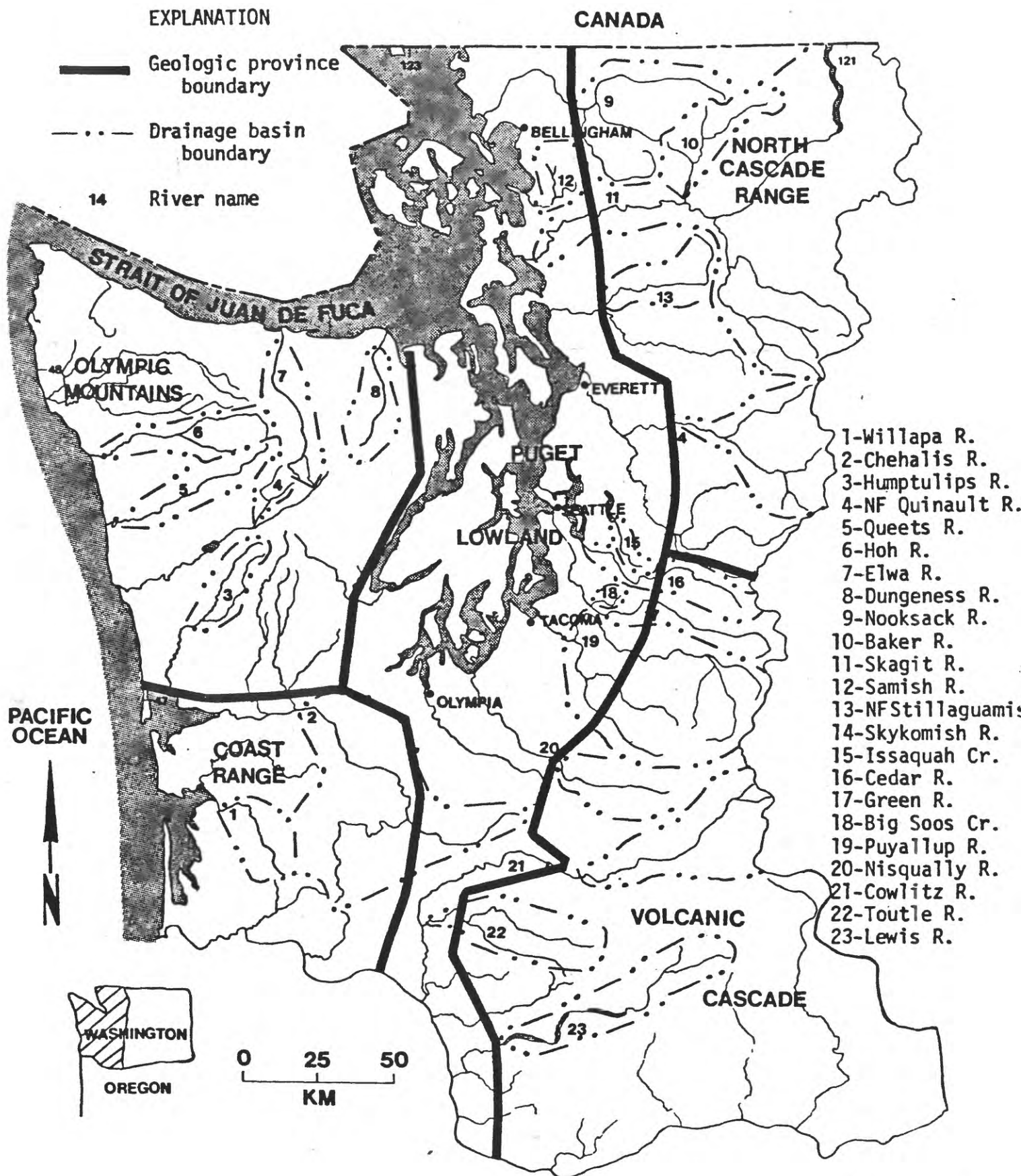


Figure 1.--Map showing selected river basins and geologic provinces (McKee, 1972) in western Washington.

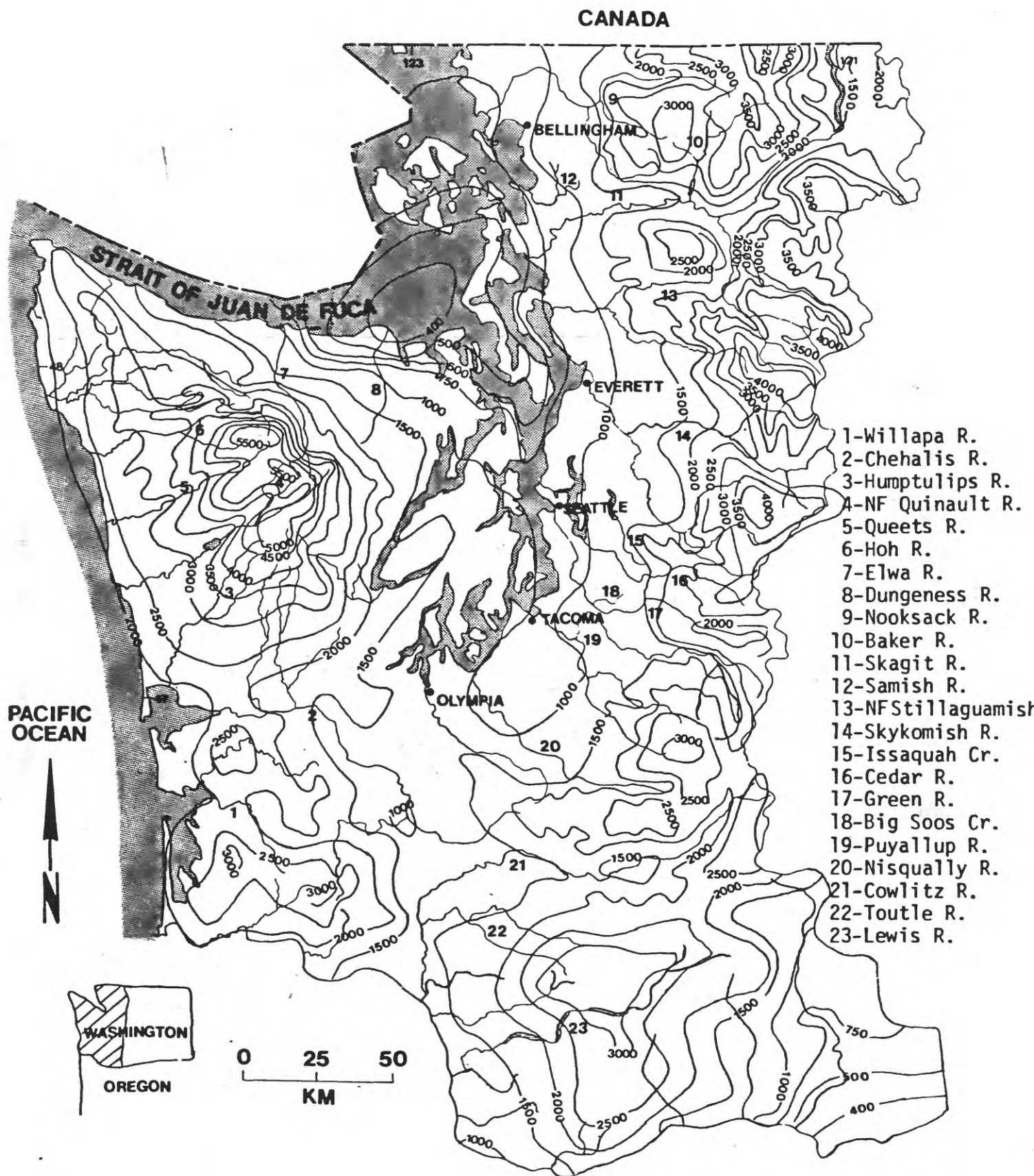


Figure 2.--Map showing mean annual precipitation, in millimeters, for western Washington (after U.S. Weather Bureau, 1965). Contour lines join points of equal mean annual precipitation.

basins because of contributions from late-melting snowfields and glaciers in alpine areas (Rasmussen and Tangborn, 1976). In the urban areas of the Puget lowland the mean annual air temperature is about 11°C and extended periods of temperatures below freezing or above 35°C are uncommon (Puget Sound Task Force, 1970). Temperature data are sparse at higher elevations, but measured lapse rates of about 5.5°C/km suggest that mean temperature is about 5.5°C and 2.82°C at elevations of 1000 and 1500 m, respectively (Porter, 1977). Only small areas (<5 percent) of most drainage basins lie above 1500 m elevation, but snow and ice melt from these zones may provide as much as 30 percent of the late summer discharge in rivers draining the Cascade and Olympic Mountains (Tangborn and Rasmussen, 1976).

When white settlers first arrived, the natural vegetation of western Washington was dominated by thick, old-growth coniferous forests. Deciduous trees grew along floodplains, and prairie vegetation and alpine tundra covered minor areas. Present cover consists mainly of successional coniferous forests. Old-growth forests are confined to wilderness and park areas, and to high-elevations zones. Franklin and Dyrness (1973) provide a complete description of the vegetation and vegetation zones of the Pacific Northwest.

Geology

The geology of western Washington was reviewed by McKee (1972), and the boundaries of the geologic provinces shown in figure 1 are modified from his work. Figure 3 shows the generalized geology of western Washington and table 1 lists the major rock types that are present in each of the geologic provinces. Unaltered to altered volcanic rocks and marine and continental sedimentary rocks, metamorphosed to zeolite facies (Stewart, 1974), comprise the dominant lithologies in western Washington. Higher-grade metamorphic and plutonic rocks are exposed in some parts of the North Cascade Range, and in limited areas of the Volcanic Cascades. The San Juan Islands consist of altered volcanic and metamorphic rocks, but no major rivers drain the islands.

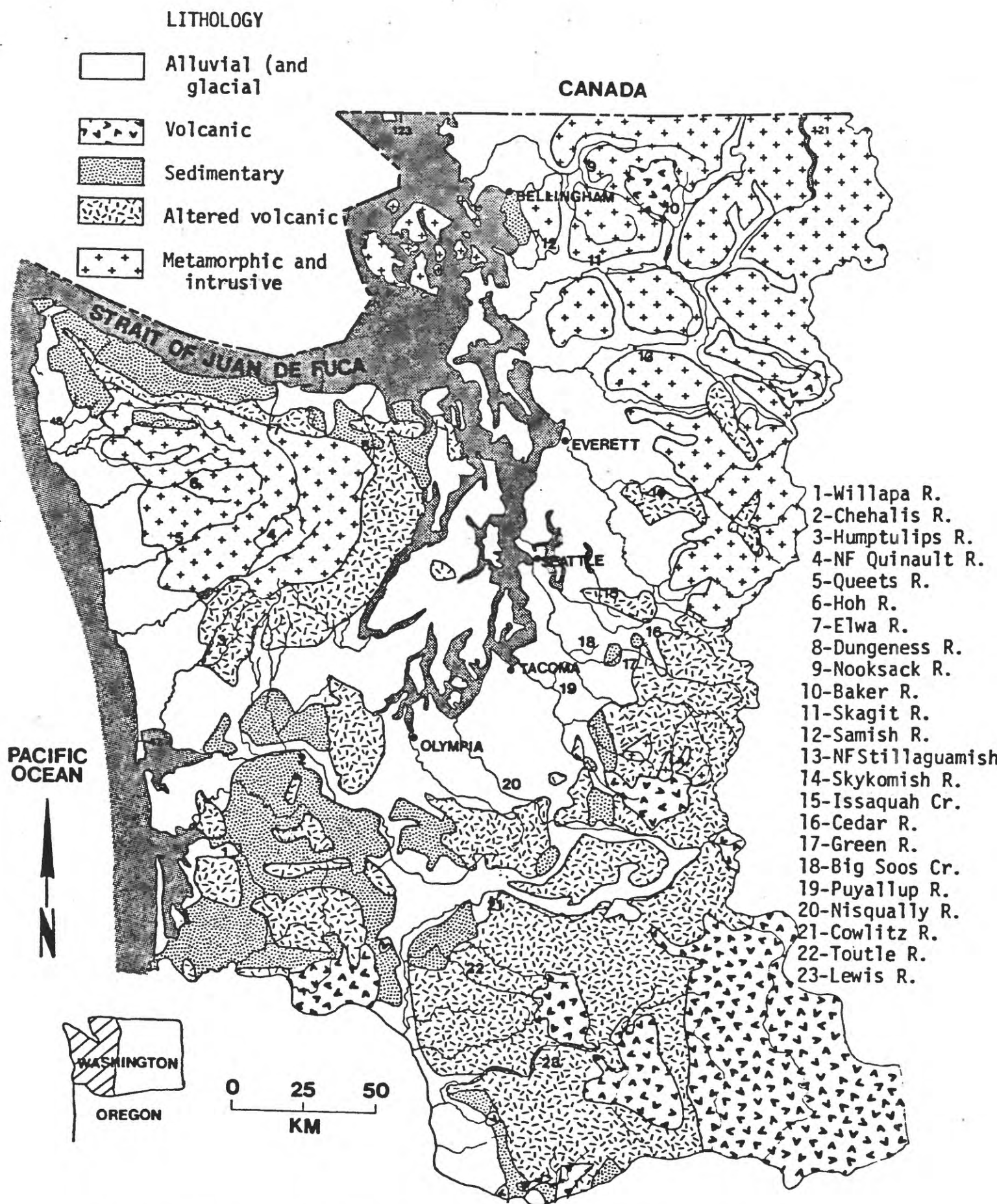


Figure 3.--Generalized geology of western Washington (after McKee, 1972).

Table 1.--Generalized description of rock types in western Washington.

Geologic province	Rock type
Coast Range	Sedimentary rocks (graywacke), minor volcanic rocks (basalt).
Olympic Mountains	Sedimentary rocks (graywacke and shale) and volcanic rocks (basalt).
North Cascade Range	Metamorphic (including restricted areas of carbonate rocks) and granitic rocks; volcanic rocks at Mount Baker and Glacier Peak; isolated areas of ultramafic rocks, principally in the Nooksack River drainage basin; glacial and alluvial deposits (mixed rock types) mantle bedrock slopes below about 1400 m elevation, and comprise thick fills in most river valleys.
Puget lowland	Glacial and alluvial deposits (mixed rock types) as much as 1000 m thick mantle most of the lowland; sedimentary and volcanic rocks lie at or near the surface in the eastern portion of the area.
Volcanic Cascades	Altered older (mid-Tertiary) volcanic and young (Quaternary) volcanic rocks (generally andesites); sedimentary rocks cover extensive areas, particularly in the Green, Cowlitz, and Toutle River drainage basins.

Readily soluble minerals are generally uncommon in the silicate rocks of western Washington. Restricted areas of limestone and marble in the North Cascade Range (see Misch, 1977), and extensive calcite-veining and minor gypsum in the volcanic rocks of the Olympic Mountains (Rau, 1973; Larson, 1979) are notable exceptions. In addition, analyses from certain springs that flow from marine sedimentary rocks (Luzier, 1969) suggest contributions from sodium-chloride brines, which probably represent relict sea-water. Thermal springs on the cones and flanks of the active Cascade volcanoes (see Frank, 1981) may also contribute more highly mineralized waters to streams and rivers. With these exceptions, however, the flux of inorganic constituents to surface waters in western Washington results from weathering of silicate minerals in surface and near-surface environments (see Wildrick, 1976).

METHOD AND DATA ANALYSIS

In the 1950s, the U.S. Geological Survey began extensive chemical sampling of selected western Washington rivers. In the early 1960s, the number of rivers sampled on a regular basis was expanded. University investigators, and other Federal, State, and municipal agencies have also conducted extensive sampling and analysis programs on some rivers, but the most detailed long-term records of inorganic water quality have been collected over the past 20 years by the Geological Survey. The record, however, is not uniform. Years of no analyses or missing analyses, major changes in sampling locations and measurement techniques, and changes in sampling frequency are found in some of the best long-term records. The National Stream Quality Accounting Network (NASQAN) was established by the Geological Survey in 1972, in part to assure regular measurement of uniform water-quality characteristics throughout the United States. NASQAN stations were first established in western Washington in 1974, and during the 1980 water year (October 1979 through September 1980) nine NASQAN stations were in operation in this region. The hydrologic-benchmark program (Cobb and Biesecker, 1971), designed to provide hydrologic data from rivers which drain undisturbed basins, operates one station, North Fork Quinault River at Amanda Park, in western Washington. The two programs provide continuity for water-quality measurements at certain sites over the past 7 years. These data, in addition to less complete measurements collected since 1961, form the data base for this report.

Annual summaries of chemical data collected by the Geological Survey for surface waters are printed in the Water Data for Washington series (U.S. Geological Survey, 1961-1980) and stored in the USGS WATSTORE computer files. These data and hydrologic and chemical data collected by other agencies in Washington are stored in the Environmental Protection Agency's STORET computer files.

Twenty-three rivers were chosen for analysis after examination of all existing records for Washington. In general, the criteria used for river selection included: (1) at least 3 years of records at the same or nearby gage; (2) discharge and chemical data available for at least 25 samples; (3) drainage area of more than 100 km² above the sample site; and (4) no major diversions above sample site. Only one record was chosen where more than one sample site existed on a river. All stations listed in Appendix A meet these criteria; most stations have at least 50 samples in the 1961-80 period, and the Puyallup River at Puyallup record includes about 190 samples.

Selected drainage basins cover the complete range of geologic terranes and climates included in the provinces. Runoff ranges from about 660 to 4000 millimeters and mean annual discharge varies from 3.6 to 473 m³/sec. However, coverage was not uniform among the provinces and several rivers with acceptable data records according to the criteria were not included because basin characteristics (primarily geology and precipitation) were similar to basins included in Appendix A. Water-chemistry records at most stations began in the 1960s and continued on an irregular basis until the NASQAN program was instituted in the mid-1970s, but lack of discharge measurements limits the utility of some of these early records. With the exception of the Snohomish River station, all active NASQAN stations were included.

Dissolved calcium, magnesium, sodium, potassium, sulfate, chloride, and silica are evaluated in this study. Unpublished summary values for pH and bicarbonate given in Leibbrand (1970) for the same stations are also included in a separate analysis. Throughout the period, water samples were analyzed by standard methods (Brown, Skougstad, and Fishman, 1970; Skougstad et al, 1979). Though these analytical techniques changed over the ~~20~~^{year} period of interest, the chemical data should be comparable over the entire period, with the possible exception of low-level chloride and sulfate analyses. Records for the dissolved constituents of interest are generally good. However, a paucity of silica analyses and several years of sparse sulfate analyses in the 1968-74 period make the data set for these variables less complete.

Data for discharge and dissolved constituents were evaluated by regression analyses to test for relationships between discharge and concentration. A Tektronix PLOT 50 statistical package was used, which regresses original and transformed data according to eight different models. All data were first screened by eliminating zero values that were obvious typographical or analytical errors and non-zero "mistakes" --values more than four standard deviations removed from the mean. The regression equations by which discharge explained the highest percent of the variance (R^2) in constituent concentrations were selected. For significant regression relationships ($\alpha = 0.05$) constituent concentrations at mean annual discharge were calculated for comparison between rivers and to evaluate ratios of major ions. If regression relationships were not significant, arithmetic mean values were calculated; this was often the case for potassium, chloride, and silica, which are related in a complex way to discharge (Kennedy and Malcom, 1978).

RESULTS

Summaries of statistics and discharge/concentration analyses for each of the 23 rivers are given in Appendix B; data derived from these calculations are summarized in this section. Mean concentrations and the observed range in values, grouped by geologic province, are given for each variable in table 2. Table 3 lists ratios of selected dissolved ions, and the weight proportions of major cations and anions for the study rivers. These average values are based on a small number of rivers in each province, may not be representative, and should be regarded only as estimates of average concentrations in rivers of that province.

Average dissolved concentrations of cations and anions were low and pH was nearly neutral for most rivers. The river waters are mainly dilute solutions of calcium- or calcium-sodium bicarbonate; dissolved silica concentrations generally equaled or exceeded calcium concentrations. Potassium concentrations seldom exceeded 1 mg/L in any of the records, and dissolved magnesium levels were usually less than 2 mg/L. The proportion of calcium, sodium, and magnesium, calculated as weight percent, are plotted in figure 4. The calcium proportion exceeded 39 percent in all cases, and accounted for more than 50 percent in most rivers, though proportions of calcium and sodium varied considerably among the 23 drainage basins. Bicarbonate, sulfate, and chloride, the principal anions, are shown in figure 5. Dissolved bicarbonate accounted for more than 75 percent of the total anions in most rivers. Sulfate comprised more than 15 percent of the anion total in seven rivers and chloride exceeded 10 percent in only 2 of 23 drainage basins.

Table 2
Summary of data for 23 rivers draining western Washington

Geologic province	Number of rivers	Total drainage area, in km ²	Dissolved constituents and pH	Concentration, in mg/L	
				Mean ^a	Range of observed values
Coast Range	2	3,688	Ca	5.2	2.9- 9.0
			Mg	1.6	0.4- 3.4
			Na	4.8	2.7- 8.4
			K	0.6	0.1- 1.8
			HCO ₃ ^b	25.0	10.0-49.0
			SO ₄	5.0	1.6-15.0
			Cl	4.2	0.9- 9.5
			SiO ₂	14.1	8.8-20.0
			pH ^b	7.1	6.4- 7.6
Olympic Mountains	6	3,443	Ca	10.4	3.5(S)-23.0(V)
			Mg	1.2	0.1(S)- 3.9(V)
			Na	2.2	0.9(V)- 4.4(V)
			K	0.3	0.0(V,S)- 1.9(V)
			HCO ₃ ^b	36.4	10.0(S)-79.0(V)
			SO ₄	6.8	1.6(S)-16.0(V)
			Cl	1.6	0.0(V)- 5.0(S)
			SiO ₂	5.9	1.8(V)-13.0(S,V)
			pH ^b	7.4	6.4(S)- 8.1(V)
North Cascade Range	5	11,589	Ca	6.4	2.0-12.0
			Mg	1.4	0.1- 3.8
			Na	1.5	0.6- 3.3
			K	0.5	0.2- 1.2
			HCO ₃ ^b	24.2	10.0-47.0
			SO ₄	5.0	0.3-16.0
			Cl	0.9	0.2- 3.0
			SiO ₂	6.3	3.6-10.0
			pH ^b	7.1	6.3- 8.2
Puget lowland	3	542	Ca	8.3	4.3-14.1
			Mg	2.8	1.2- 5.1
			Na	4.3	1.7- 8.7
			K	0.8	0.2- 2.1
			HCO ₃ ^b	41.0	14.0-71.0
			SO ₄	6.7	3.8-13.0
			Cl	2.5	1.2- 4.0
			SiO ₂	11.6	4.5-23.0
			pH ^b	7.1	6.3- 7.8
Volcanic Cascades	7	11,300	Ca	5.7	2.3-18.0
			Mg	1.3	0.4- 4.8
			Na	3.3	0.2-14.0
			K	0.6	0.1- 2.1
			HCO ₃ ^b	27.4	18.0-58.0
			SO ₄	3.3	0.4-12.0
			Cl	1.9	0.7-14.0
			SiO ₂	13.6	8.1-23.0
			pH ^b	7.1	6.2- 8.0

a/ Concentration at mean annual discharge, averaged for the number of rivers in the province as shown.

b/ "Mean" pH and bicarbonate values, (Leibbrand, 1970) generally for the period 1959-1967. pH is calculated as $-\log [H]$, where $[H]$ represents the hydrogen-ion activity.

c/ Highest or lowest values were measured where bedrock in drainage basin is predominantly metasedimentary (S) or metavolcanic (V).

Table 3.--Cation and anion weight percent, and element ratios, calculated for individual rivers at mean annual discharge.

River	Weight percent, calculated to 100 percent		$\frac{[Na]}{[Cl]}^b$	Ratios		
	Ca/Mg/Na	HCO ₃ /SO ₄ /Cl ^a		$\frac{Ca}{Mg}$	$\frac{Ca}{SO_4}$	$\frac{SO_4}{Cl}$
Willapa	39/12/49	73/13/15	1.7	3.2	0.8	1.1
Chehalis	49/15/36	80/8/12	1.8	3.2	1.2	1.3
Humptulips	57/14/29	85/8/7	1.8	4.1	1.9	1.2
NF Quinault	85/4/10	----	2.1	20.4	1.4	8.4
Queets	68/8/24	74/20/6	1.4	8.3	1.0	2.5
Hoh	78/7/15	76/21/3	1.7	11.6	1.2	4.8
Elwha	80/8/12	84/15/1	2.9	10.5	1.6	7.6
Dungeness	76/11/13	88/11/1	3.9	7.1	2.3	6.7
Nooksack	69/19/12	78/20/2	2.8	3.5	1.2	9.0
Baker	73/12/15	73/25/2	3.0	6.5	1.0	11.0
Skagit	72/14/14	85/13/2	2.6	5.2	1.5	6.0
Samish	59/17/24	82/13/5	1.7	3.4	1.4	2.0
NF Stillaguamish	64/18/18	87/9/4	2.4	3.7	2.1	2.7
Skykomish	65/9/26	82/12/6	2.4	6.8	1.8	2.1
Issaquah	52/19/29	82/13/5	1.9	2.8	1.3	2.6
Cedar	64/13/23	88/9/3	1.8	4.9	2.2	2.7
Green	54/13/33	83/11/6	2.3	4.1	1.8	1.4
Big Soos	52/19/29	80/15/5	3.1	2.8	1.1	3.2
Puyallup	56/14/30	77/19/14	2.9	3.9	1.1	3.4
Nisqually	54/14/32	87/8/5	1.9	3.8	2.3	1.4
Cowlitz	61/10/29	90/7/3	4.3	5.9	3.2	1.8
Toutle	45/12/43	83/7/10	1.8	3.9	1.4	0.9
Lewis	52/12/36	90/6/4	2.5	4.3	1.7	1.4

a/ From Leibbrand (1970); coverage is generally for the period 1959-1967.

b/ Brackets denote activities; other ratios are of concentrations.

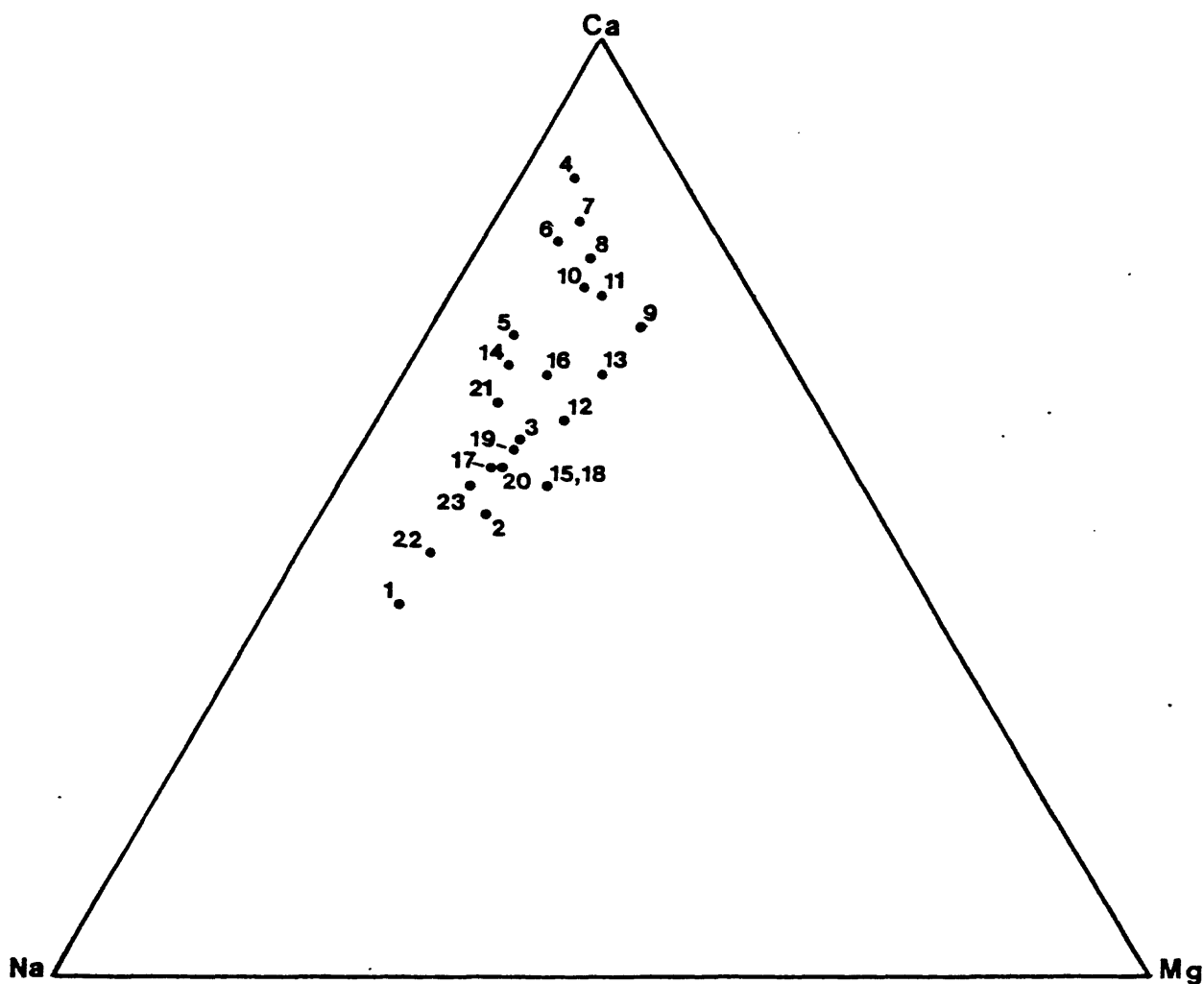


Figure 4.--Triangular diagram showing the relative proportion of dissolved calcium, sodium, and magnesium present at mean annual flow in 23 western Washington rivers. Number correspond to rivers shown in figure 1; more detailed information is provided in Appendix A.

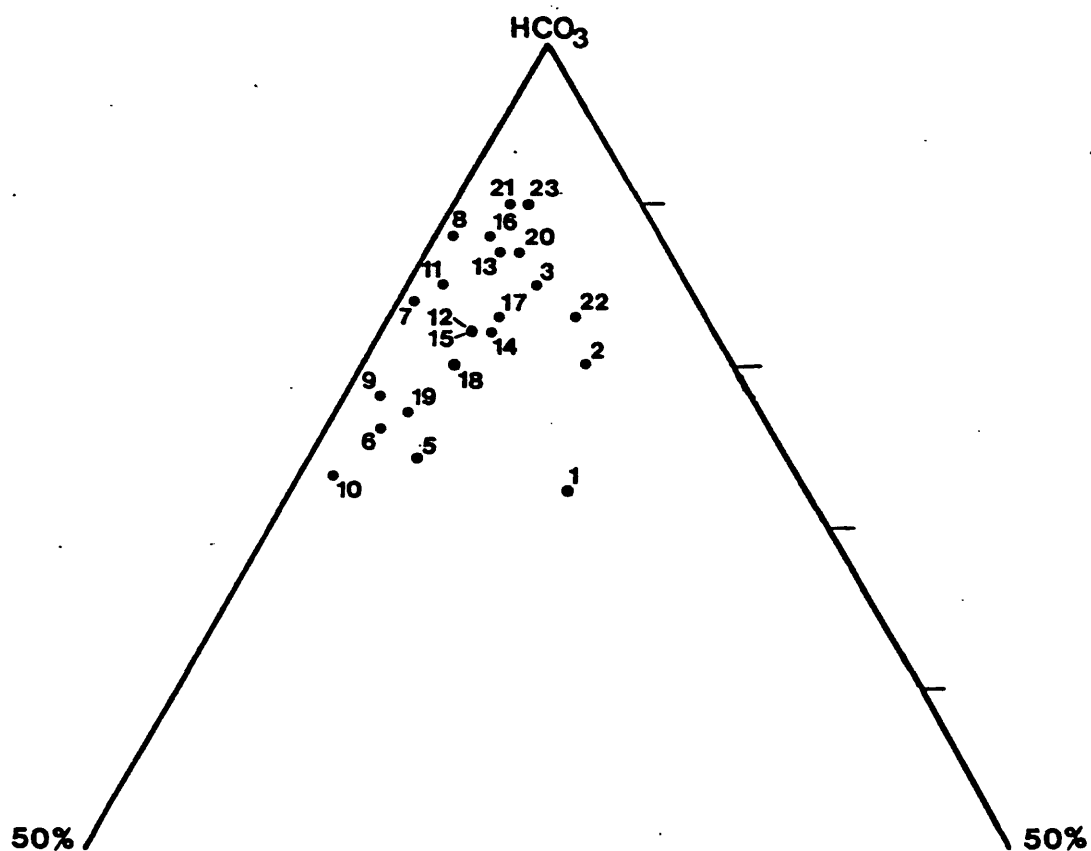
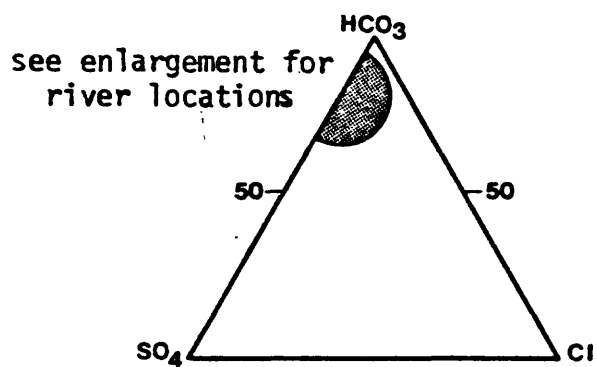
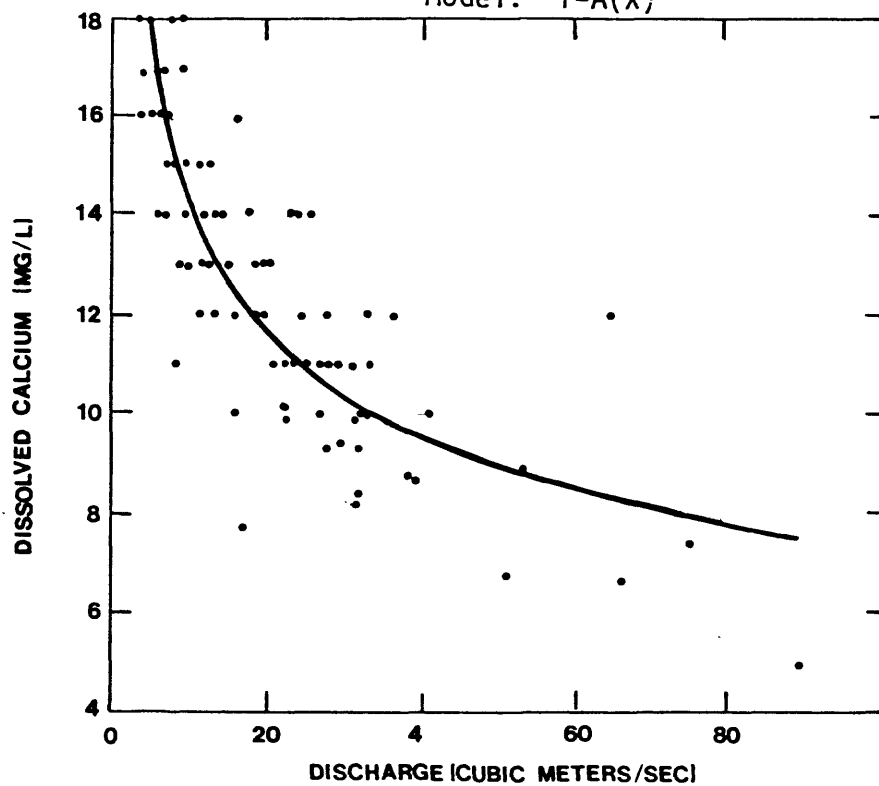


Figure 5.--Triangular diagram showing the relative proportion of dissolved bicarbonate (average values of Leibbrand, 1970), sulfate, and chloride present at mean annual flow in 23 western Washington rivers. Numbers correspond to rivers shown in figure 1; more detailed information is provided in Appendix A.

North Fork Quinault River near Amanda Park 12039300

Model: $Y=A(X)^B$

A



North Fork Quinault River near Amanda Park 12039300

Scatter Plot

B

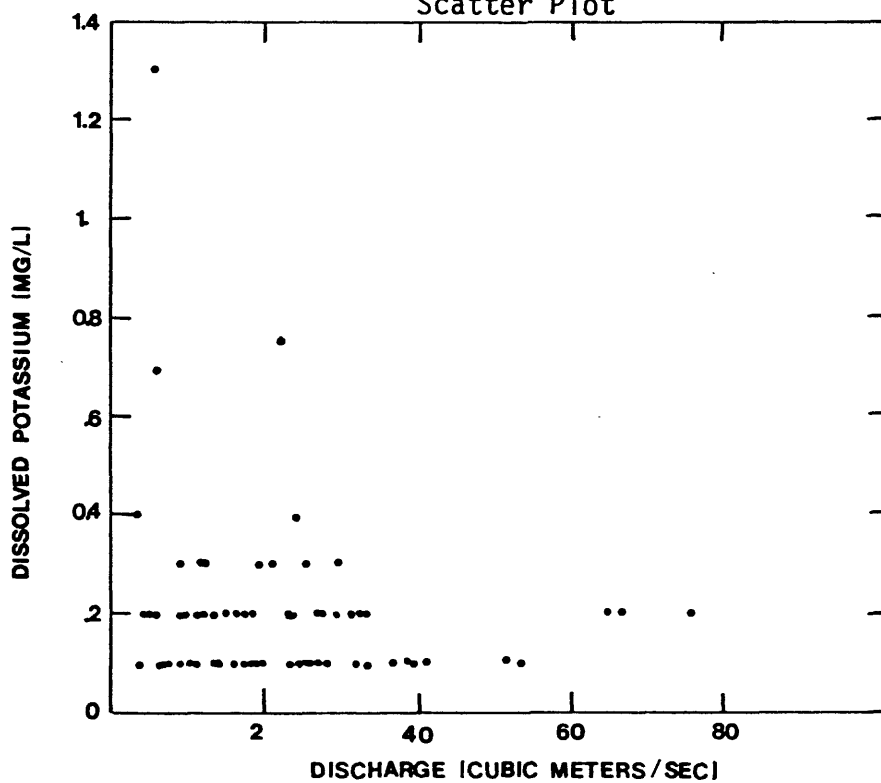


Figure 6.--Plots of discharge/dissolved cation relations in the North Fork Quinault River. (A) Discharge vs. calcium; (B) discharge vs. potassium.

The relationships between dissolved constituents and discharge varied significantly from basin to basin, and among constituents at a station. In many cases logarithmic transformation of one or both variables resulted in the best correlations. However, at some stations linear relationships resulted in the highest R^2 values (see Appendix B). Figure 6a shows a typical discharge versus dissolved calcium plot; the best correlation for these data ($R^2 = 0.69$) results from log-transforming both variables. Figure 6b is a scattergram of potassium vs. discharge for the same river; discharge does not explain any of the variance in dissolved potassium concentration. Although figure 6b is a particularly clear example, discharge and potassium are generally not highly correlated in western Washington rivers. The percent variance explained by regression relationships for other dissolved constituents generally lies between these extremes.

Discharge explains more than 80 percent of the variance in calcium and sodium concentrations for about 20 percent of the rivers, and more than 50 percent of the variance in calcium levels for 17 of the 23 rivers (table 4). Dissolved levels of the other constituents listed in table 4 are not as highly correlated with discharge, and in only two rivers is more than 50 percent of the potassium variance explained by discharge. The anions sulfate and chloride are not strongly correlated with discharge at many stations; the highest R^2 values are 0.69 (Cowlitz River) and 0.67 (Green River), respectively (see Appendix B). Bicarbonate was not included in the regression analyses because it is not a component of silicate rocks, but it is probably strongly correlated with discharge because it is the major anion that balances calcium, and calcium is strongly correlated with discharge. Although dissolved silica concentrations display relatively little variation over a range of discharge (see silica values in table 2), discharge is significantly correlated with silica at almost half the study stations.

Steele and others (1974) showed that specific conductance is strongly correlated with dissolved concentrations of most major ions in streamwater, particularly when the range in specific-conductance values is large. This approach has not been used in the present study. However, specific conductance is strongly correlated with dissolved calcium, bicarbonate, sulfate, and sodium--the major carriers of charge --in many of the 23 rivers (Dethier, unpublished data), and these relationships should be studied in detail.

Table 4.--Concentration versus discharge regression equations:
percent variance explained.

Dissolved constituent	Percent ¹ of regression equations for which $R^2 \geq$		
	0.2	0.5	0.8
Ca	87	74	22
Mg	70	39	9
Na	74	43	17
K	26	9	--
SO ₄	48	17	--
Cl	39	17	--
SiO ₂	48	22	4

1/ N = 23. Two stations lie immediately downstream from dams and show no relationship between discharge and dissolved levels of any constituent; several other rivers have major upstream impoundments.

DISCUSSION

The mean concentrations and range of values for dissolved constituents are broadly similar in all study rivers, and only calcium concentrations are consistently correlated with variations in discharge. Differences in rock type probably contribute to variations in surface-water chemistry between geologic provinces, and to specific chemical characteristics in some drainage basins. However, more detailed examination of bedrock mineralogy, the characteristics of chemical weathering, and hydrologic pathways--beyond the scope of this study--are required for interpretation of the processes controlling surface-water chemistry of specific drainage basins.

Behavior of Specific Ions

Calcium and potassium concentrations illustrate the range of relations between dissolved inorganic and discharge typically found in western Washington rivers. In most of the 23 rivers, the highest concentrations of potassium are less than 1 mg/L, and the extreme value for all rivers (1961-80, N = 1450) is 2.1 mg/L. Average and extreme calcium values are almost an order of magnitude higher (see table 2). Variations in potassium concentration are correlated with discharge in only a few rivers, whereas calcium values show a significant correlation to discharge in most of the sample rivers. Because Ca/K ratios in most noncarbonate rocks average 1-6:1 (Krauskopf, 1967) in contrast to 10:1

in river waters, potassium is "conserved" with respect to calcium. Potassium release to surface waters in western Washington are controlled by incongruent weathering, selective sorption by secondary minerals, and biological uptake. Potassium is an essential nutrient for vegetative growth. Biologic uptake thus exerts a strong control on surface-water concentrations of dissolved potassium (see also Slack and Feltz, 1968; Larson, 1979; Feller, 1977), although weathering and specific sorption influence waters that pass below the root zone. Calcium must also be influenced by both biological and geochemical processes. In contrast to potassium, however, biological requirements for calcium are small compared to the quantities released to soil solutions by weathering reactions (Cole, Gessel, and Turner, 1973), and calcium persists at relatively high concentrations in surface waters.

Sulfate is an important nutrient that is released by mineral weathering and contributed in precipitation. However, it is not strongly sorbed by organic matter or most secondary minerals, and its concentration in surface waters reflects a balance between precipitation input, chemical weathering, and biological uptake.

Magnesium, like calcium, is an important nutrient which competes for exchange sites on clay minerals and organic matter. Most rocks in western Washington contain low concentrations of magnesium, and this is reflected by low (1-2 mg/L) levels in most surface waters.

Neither sodium nor chloride are used extensively by vegetation; sodium may exist on exchange sites in soil or weathered material, but it is readily displaced by the hydrogen ion or other cations. Chloride exhibits only minor exchange properties. Springs rich in sodium and chloride contribute to surface waters in basins that drain sedimentary rocks, thus surface-water concentrations of these ions reflect the amount contributed by precipitation, mineral weathering, and as flow from springs.

Geologic Provinces

Average river chemistry (see table 2) indicates distinct differences among the geologic provinces, particularly for dissolved calcium, chloride, and silica. Other dissolved constituents show distinct anomalies in certain of the provinces, but no general pattern is apparent. Over the period examined all rivers were chemically dilute and pH values were near neutral. Rivers that drained the North Cascade Range were the most dilute, whereas dissolved concentrations were highest in the Puget lowland, and in the six rivers that flow from the Olympic Mountains. The percentages and ion ratios listed for individual rivers in table 3 help to illustrate the differences in river chemistry that result in the average values of table 2.

The highest calcium concentrations, and some of the highest Ca/Mg and SO_4/Cl ratios were found in rivers draining the Olympic Mountains (tables 2 and 3). Calcite and minor amounts of gypsum comprise vein material in altered volcanic and sedimentary rock of the Olympic Mountains (Larson, 1979) and dissolution of these two minerals probably accounts for the high calcium and sulfate concentrations. Sulfide minerals such as pyrite may also contribute to relatively high sulfate levels. Chloride and silica concentrations are low in rivers draining the Olympic Mountains and the North Cascade Range. Low silica values suggest that rock-water contact times are relatively short and that readily soluble silica compounds are not abundant. Rivers draining the other provinces contain considerably more silica in low runoff areas like the Puget lowland, and in wet areas like the Volcanic Cascades. The higher silica concentrations probably reflect the abundance of relatively soluble minerals and glass.

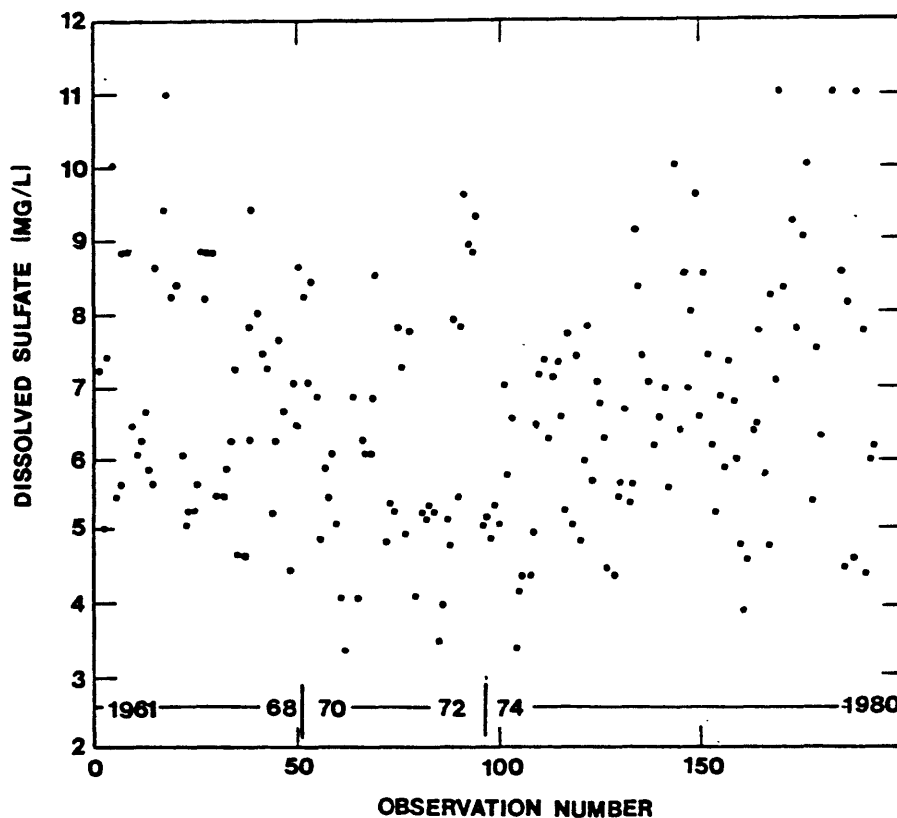
Chloride concentrations are high in the Coast Range province, and in rivers like the Green and Toutle, both of which drain extensive areas of marine sedimentary rocks in the Volcanic Cascades province. Sodium-chloride springs flow into the Green and Toutle Rivers, and sodium is strongly correlated with chloride in these rivers (see Appendix B). Similar springs may also contribute to the Coast Range drainages, but published information is lacking.

Sulfate concentrations and elemental ratios in some rivers suggest certain unique sources for this anion. High SO_4/Cl ratios characterize the Nooksack, Baker, and Skagit Rivers in the North Cascade Range. However, calcium concentrations and Ca/Mg ratios are not high. Sulfate-rich water from the vicinity of Mount Baker's Sherman Crater (Bortleson et al, 1976) is the likely source of high sulfate concentrations in the Baker and Skagit Rivers. Thermal springs may contribute sulfate to the Nooksack River, but drainage from old mines and weathering of sulfide ores (Moen, 1962) are also potential sources. Concentrations of sulfate are relatively high in these rivers, in rivers draining the Olympic Mountains and some Puget Sound lowland rivers, but are relatively low in other western Washington rivers.

Potential Detection of Trends

Increasing sulfate levels at the Baker River station were probably caused by renewed thermal activity in Sherman Crater which began in March 1975 (Frank et al, 1977). Unfortunately, the long-term record at this station is not sufficient to demonstrate a trend, or a sharp change in sulfate levels. Long, detailed records from the Puyallup and Chehalis Rivers (fig. 7), however, show a divergent trend. The length and detail of the two records are similar, but sulfate concentrations in the Chehalis increased steadily and their variability increased dramatically after about 1975. No significant change is apparent in the Puyallup record. It seems unlikely that a regional influence such as acid rain would affect the Chehalis without affecting the Puyallup River. A point source of pollution, perhaps mine drainage, sewage, or an industrial outfall, therefore may be responsible. The absence of records for the important years 1969 and 1970 makes it difficult to specify the exact timing or nature of the change. For these two rivers, the importance of the pre-NASQAN record cannot be underestimated, and it is unfortunate that comparable records are apparently unavailable for other western Washington rivers. If NASQAN-type monitoring continues, detection of long-term trends and "step" changes will become possible for more rivers in this area.

Puyallup River at Puyallup, Washington 12101500



Chehalis River at Porter, Washington 12310000

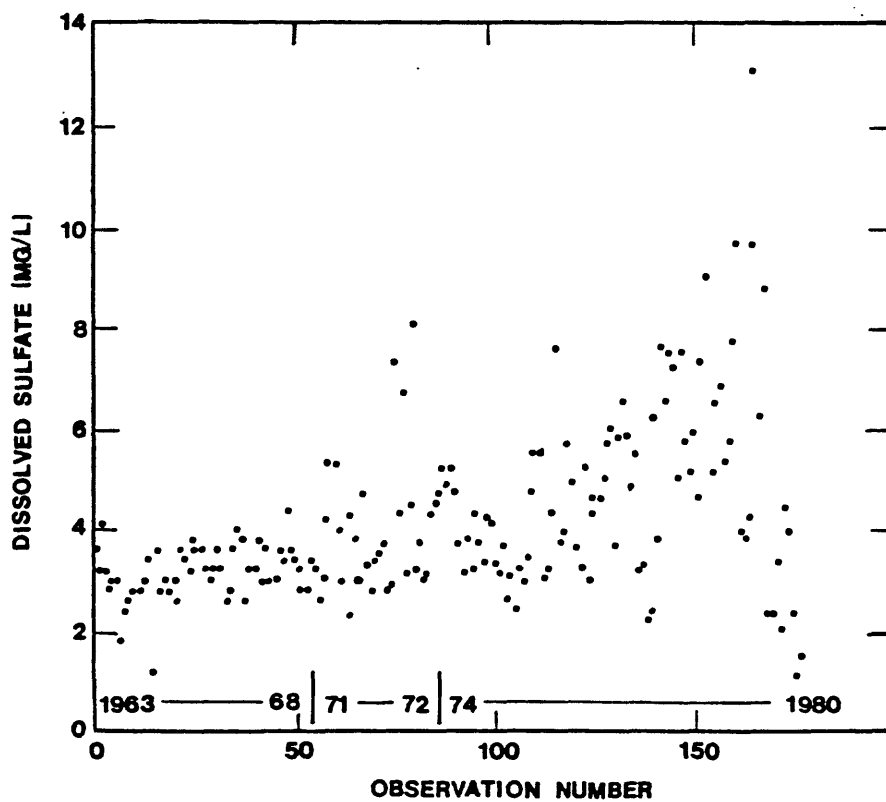


Figure 7.--Scatter plots of measured sulfate concentration vs. time for the Puyallup and Chehalis Rivers.

SUMMARY

Generally dilute concentrations and neutral pH levels characterized 23 rivers in western Washington during the period 1961-1980. Calcium and, to a lesser extent, sodium were the dominant cations, whereas bicarbonate accounted for more than 75 percent of the total anion concentration in most rivers. Silica levels were higher than calcium concentrations in most cases. Discharge explained a significant amount of variance in calcium concentrations for most rivers (and probably bicarbonate--which was not evaluated), and discharge and sodium concentrations were significantly correlated for many rivers. Other dissolved constituents evaluated, however, were more poorly correlated with discharge. Relatively high levels of calcium and sulfate in waters from the Olympic Mountains suggest contributions from the dissolution of calcite and gypsum which is present in altered volcanic rocks. Elevated chloride levels in some rivers are apparently associated with areas of marine sedimentary rocks. Silica concentrations in Olympic and North Cascade rivers are considerably lower than those found in the other study rivers. Studies of the geochemistry and hydrology of small catchments are required to better understand the processes controlling chemical characteristics of surface waters in western Washington.

REFERENCES CITED

- Bortleson, G. C., Wilson, R. T., and Foxworthy, B. L., 1976, Water-quality effects on Baker Lake of recent volcanic activity at Mount Baker, Washington: U.S. Geological Survey Professional Paper 1022-B, 30 p.
- Brown, E., Skougstad, M. W., and Fishman, M. J., 1970, Methods for collection and analysis of water samples for dissolved minerals and gases: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, 160 p.
- Cobb, E. D., and Biesecker, J. E., 1971, The national hydrologic benchmark network: U.S. Geological Survey Circular 460-D, 38 p.
- Cole, D. W., Gessel, S. P., and Turner, J., 1973, Elemental cycling and even-age forest management, *in* Hermann, R. K., and Lavender, D. P., eds., Even-Age Management: Corvallis, Oregon State University, 250 p.
- Drost, B. W., and Lombard, R. C., 1978, Water in the Skagit River Basin, Washington: U.S. Geological Survey Water-Supply Bulletin 47, 247 p.
- Federal Interagency Work Group on precipitation quality, 1978, Research and monitoring of precipitation chemistry in the United States--present status and future needs: U.S. Government Printing Office 679-010/22, 64 p.
- Feller, M. C., 1977, Nutrient movement through western hemlock-western redcedar ecosystems in southwestern British Columbia: Ecology, v. 58, p. 1269-1283.

- Frank, David, 1981, Origin, distribution, and rapid removal of hydrothermally formed clay at Mount Baker, Washington: U.S. Geological Survey Professional Paper (in press).
- Frank, David, Meier, M. F., and Swanson, D. A., 1977, Assessment of increased thermal activity at Mount Baker, Washington, March 1975-March 1976: U.S. Geological Survey Professional Paper 1022-A, 49 p.
- Franklin, J. F., and Dyrness, C. T., 1973, Natural vegetation of Oregon and Washington: U.S. Department of Agriculture Forest Service General Technical Report PNW-8, 417 p.
- Kennedy, V. C., and Malcom, R. L., 1978, Geochemistry of the Mattole River of northern California: U.S. Geological Survey Open-File Report 78-205, 324 p.
- Krauskopf, K. B., 1967, Introduction to geochemistry: New York, McGraw-Hill, 721 p.
- Larson, A. G., 1979, Origin of the chemical composition of undisturbed forested streams western Olympic Peninsula, Washington State (Ph. D. thesis): Seattle, University of Washington, 216 p.
- Leibbrand, N. F., 1970, Chemical quality of surface waters in Washington: U.S. Geological Survey unpublished manuscript, 200 p.
- Luzier, J. E., 1969, Geology and ground-water resources of southwestern King County, Washington: Washington Department of Water Resources Water-Supply Bulletin 28, 260 p.
- McKee, Bates, 1972, Cascadia--the geologic evolution of the Pacific Northwest: New York, McGraw-Hill, 394 p.

- Misch, Peter, 1977, Bedrock geology of the North Cascades, Field Trip No. 1, *in* Brown, E. H., and Ellis, R. C., eds., Geological Excursions in the Pacific Northwest: Bellingham, Guidebook Geological Society of America 1977 Annual Meeting, p. 1-62.
- Moen, Wayne S., 1962, Geology and mineral resources of the north half of the Van Zandt quadrangle, Whatcom County, Washington: Washington Department of Natural Resources Division of Mines and Geology Bulletin 50, 129 p.
- Porter, S. C., 1977, Present and past glaciation threshold in the Cascade Range, Washington, U.S.A.--topographic and climate controls, and paleoclimatic implications: *Journal of Glaciology*, v. 18, p. 101-116.
- Puget Sound Task Force Hydrologic Studies Technical Committee, 1970, Comprehensive study of water and related land resources, Puget Sound and adjacent waters, State of Washington--Appendix III, Hydrology and natural environment: Vancouver, Washington, Pacific Northwest River Basins Commission.
- Rasmussen, L. A., and Tangborn, W. V., 1976, Hydrology of the North Cascades Region, Washington 1--Runoff, precipitation, and storage characteristics: *Water Resources Research*, v. 12, p. 187-202.
- Rau, W. W., 1973, Geology of the Washington coast between Point Grenville and the Hoh River: Washington Department of Natural Resources Bulletin 66, 58 p.
- Santos, J. F., and Stoner, J. D., 1972, Physical, chemical, and biological aspects of the Duwamish River estuary, King County, Washington, 1963-67: U.S. Geological Water-Supply Paper 1873-C, 74 p.

- Skougstad, Marvin W., and others, eds., 1979, Methods for determination of inorganic substances in water and fluvial sediments: U.S. Geological Survey Techniques of Water-Resources Investigations, Book 5, Chapter A1, 626 p.
- Slack, J. R., Hirsch, R. M., and Smith, R. A., 1981, A study of trends in dissolved solids measurements at stations in the NASQAN network: unpublished manuscript.
- Slack, K. V., and Feltz, H. R., 1968, Tree leaf control on low flow water quality in a small Virginia stream: Environmental Science and Technology, v. 2, p. 126-131.
- Smith, R. A., Hirsch, R. M., and Slack, J. R., 1981, A study of trends in total phosphorus measurements at stations in the NASQAN network: U.S. Geological Survey Water-Supply Paper (in press).
- Steele, T. D., Gilroy, E. J., and Hawkinson, R. O., 1974, An assessment of areal and temporal variations in streamflow quality using selected data from the National Stream Quality Accounting Network: U.S. Geological Survey Open-File Report 74-217, 210 p.
- Stewart, R. J., 1974, Zeolite facies metamorphism of sandstone in the western Olympic Peninsula, Washington: Geological Society of America Bulletin, v. 85, p. 1139-1142.
- Tangborn, W. V., and Rasmussen, L. A., 1976, Hydrology of the North Cascades Region, Washington 2--A proposed hydrometeorological streamflow prediction method: Water Resources Research, v. 12, p. 203-216.

- U.S. Weather Bureau, 1965, Mean annual precipitation, 1930-57, State of Washington: Portland, U.S. Soil Conservation Service Map M-4430.
- Welch, E. B., 1969, Factors initiating phytoplankton blooms and resulting effects on dissolved oxygen in Duwamish River estuary, Seattle, Washington: U.S. Geological Survey Water-Supply Paper 1873-A, 62 p.
- Wildrick, L. L., 1976, Geochemical equilibria in Pleistocene sediments of the southeast Puget Sound drainage basin (M.S. thesis): Seattle, University of Washington, 78 p.
- U.S. Geological Survey, 1964, Water-quality records in Washington: Tacoma, report, 227 p.
- _____ 1965-74, Water resources data for Washington, Part 2, Water-quality records 1964-1973: Tacoma, reports published annually.
- _____ 1966-81, Water resources data for Washington, Water Years 1966-80, volume 1, western Washington: Water-Data Report WA series, 1966-81.

Appendix A.--Water chemistry on selected rivers in western Washington, 1961-1980.

Name	Station Number	Geologic province ^a	Drainage area, in km ²	Runoff, in mm	Mean annual discharge, in m ³ /s
1 Willapa River near Willapa (NASQAN)	12013500	CR	337	1,722	18.4
2 Chehalis River at Porter (NASQAN)	12031000	CR	3,351	1,109	117.8
3 Humptulips River at Humptulips	12039003	OM	342	3,550	37.9
4 North Fork Quinault River near Amanda Park (Hydrologic-Benchmark)	12039300	OM	191.9	4,008	24.4
5 Queets River near Clearwater (NASQAN)	12040500	OM	1,153	3,198	116.8
6 Hoh River at U.S. Highway 101, near Forks (NASQAN)	12041200	OM	655	3,415	70.9
7 Elwha River at McDonald Bridge, near Port Angeles (NASQAN)	12045500	OM	697	1,929	42.6
8 Dungeness River near Sequim	12048600	OM	404	862	11.0
9 Nooksack River at Deming	12210500	NC	1,513	1,972	94.6
10 Baker River at Concrete	12193500	NC	769	3,089	75.3
11 Skagit River near Mount Vernon (NASQAN)	12200500	NC	8,011	1,860	473.2
12 Samish River near Burlington	12201500	PL	227	955	6.87

Appendix A.--Water chemistry-continued.

	Name	Station Number	Geologic province ^a	Drainage area, in km ²	Runoff, in mm	Mean annual discharge, in m ³ /s
13	North Fork Stilla- guamish River near Arlington	12167000	NC	679	2,495	53.7
14	Skykomish River near Gold Bar	12134500	NC	1,386	2,551	112.1
15	Issaquah Creek near mouth, near Issaquah	12121600	PL	142	959	4.31
16	Cedar River at Renton	12119000	VC	497	1,320	19.9
17	Green River at 212th Street, near Kent	12113340	VC	1,121	~1,193	42.4
18	Big Soos Creek, above hatchery, near Auburn	12112600 12112612	PL	173	662	3.62
19	Puyallup River at Puyallup (NASQAN)	12101500	VC	2,455	1,226	95.4
20	Nisqually River at McKenna	12089500	VC	1,340	~1,500	63.7
21	Cowlitz River near Randle	14233400	VC	2,668	1,712	146.6
22	Toutle River near Castle Rock	14242700	VC	1,326	~1,500	63.1
23	Lewis River at Ariel (NASQAN)	14220500	VC	1,893	2,293	137.6

a/ Provinces include Coast Range (CR), Olympic Mountains (OM), North Cascade Range (NC), Puget lowland (PL), and Volcanic Cascades (VC), and are described in table 1.

b/ Includes 2 years at 14220200.

Appendix B.--Average concentration and discharge/concentration relations for 23 rivers in western Washington.

Name	Number	Dissolved constituent	Concentration at mean annual discharge, in mg/L	N	Regression equation Q = mean annual discharge, in cubic meters/sec	R ²	Annual gross loss, in T/km ²
Willapa River near Willapa, Washington	12013500	Ca	3.92	55	LN(Ca) = 1.70 - 0.115LN(Q)	.81	6.8
		Mg	1.22	55	LN(Mg) = 0.58 - 0.132LN(Q)	.53	2.1
		Na	4.86	55	LN(Na) = 1.86 - 0.096LN(Q)	.76	8.4
		K	0.58	55	K = 0.56 + 0.28(1/Q)	.28	1.0
		SO ₄	4.74	49	nc	nc	8.2
		Cl	4.32	54	LN(Cl) = 1.57 - 0.0058lnQ	.40	7.4
		SiO ₂	12.7	48	SiO ₂ = 1/(0.077 + 8.7*10 ⁻⁵ Q)	.17	21.9
		median pH	7.1	47	nc	nc	nc
		Cl/Na	nc	54	Na = 4.01 + 0.31(Cl)	.14	nc
		SO ₄ /Ca	nc	49	Ca = 4.26 + 0.047(SO ₄)	.14	nc
Chehalis River at Porter, Washington	12031000	Ca	6.43	69	Ca = 0.743 + 8.05(1/(1+10 ⁻⁵ Q))	.77	7.1
		Mg	2.01	69	Mg = 5.18 - 0.38/LN(Q)	.69	2.2
		Na	4.73	69	Na = 11.55 - 0.819LN(Q)	.76	5.2
		K	0.69	69	K = 1.25 - 0.067LN(Q)	.16	0.8
		SO ₄	5.18	69	SO ₄ = 5.36 - 4.30*10 ⁻³ Q	.01	5.7
		Cl	4.12	69	Cl = 3.41 + 3.67(1/(1+10 ⁻⁵ Q))	.57	4.6
		SiO ₂	15.4	118	nc	nc	17.1
		mean ^a pH	7.1	75	nc	nc	nc
		Ca	5.28	35	LN(Ca) = 2.23 - 0.156LN(Q)	.79	18.5
		Mg	1.29	35	LN(Mg) = 0.60 - 0.0091(Q)	.73	4.5
Humptulips River at Humptulips	12039003	Na	2.71	35	LN(Na) = 1.33 - 0.091LN(Q)	.35	9.5
		K	0.23	35	nc	nc	0.8
		SO ₄	2.74	29	nc	nc	9.6
		Cl	2.28	35	nc	nc	8.0
		SiO ₂	9.30	23	nc	nc	32.5
		mean ^a pH	7.2	45	nc	nc	nc
		Cl/Na	nc	35	nc	nc	nc
		SO ₄ /Ca	nc	29	nc	nc	nc
		Ca	11.02	98	LN(Ca) = 3.31 - 0.285LN(Q)	.69	44.2
		Mg	0.54	96	LN(Mg) = 0.081 - 0.167LN(Q)	.12	2.2
North Fork Quinalt River near Amanda Park	12039300	Na	1.33	97	LN(Na) = 0.79 - 0.159LN(Q)	.24	5.3
		K	0.17	97	nc	nc	0.7
		SO ₄	8.11	96	LN(SO ₄) = 3.02 - 0.29LN(Q)	.52	32.5
		Cl	0.97	98	nc	nc	3.9
		SiO ₂	4.24	96	LN(SiO ₂) = 1.66 - 0.0088(Q)	.45	17.0
		median pH	nc	97	nc	nc	nc
		Cl/Na	nc	97	nc	nc	nc
		SO ₄ /Ca	nc	96	Ca = 4.80 + 0.83(SO ₄)	.58	nc
		Ca	7.06	35	LN(Ca) = 3.43 - 0.31LN(Q)	.75	22.5
		Mg	0.85	36	Mg = 0.76 + 10.28(1/Q)	.33	2.7
Queets River at Queets, Washington	12040600	Na	2.51	36	Na = 2.42 + 10.97(1/Q)	.07	8.0
		K	0.35	36	K = 0.27 + 0.00068lnQ	.13	1.12
		SO ₄	6.79	31	SO ₄ = 5.47 + 154(1/Q)	.40	21.7
		Cl	2.76	36	LN(Cl) = 0.35 + 0.14LN(Q)	.10	8.8
		SiO ₂	5.55	29	nc	nc	17.7
		median pH	7.4	34	nc	nc	nc
		Cl/Na	nc	43	Na = 3.22 + (-1.65(1/Cl))	.33	nc
		SO ₄ /Ca	nc	36	Ca = 4.83 + 0.45(SO ₄)	.42	nc
		Ca	10.24	44	Ca = 19.7 - 2.22LN(Q)	.37	35.0
		Mg	0.88	44	nc	nc	3.0
Noh River near Forks	12041200	Na	1.95	44	nc	nc	6.7
		K	0.33	44	nc	nc	1.1
		SO ₄	8.33	38	SO ₄ = 14.98 - 1.56LN(Q)	.23	28.4
		Cl	1.74	44	nc	nc	5.9
		SiO ₂	4.69	44	nc	nc	16.0
		mean ^a pH	7.3	34	nc	nc	nc
		Cl/Na	nc	44	LN(Na) = 0.47 + 0.37LN(Cl)	.41	nc
		SO ₄ /Ca	nc	38	LN(Ca) = 0.87 + 0.70LN(SO ₄)	.76	nc
		Ca	10.24	44	Ca = 2.92 + 0.92(SO ₄)	.67	nc
		Mg	0.88	44	nc	nc	3.0

Appendix B.--Average concentration-continued.

Name	Number	Dissolved constituent	Concentration at mean annual discharge, in mg/L	N	Regression equation	R ²	Annual gross loss, in T/km ²
Elwha River at McDonald Bridge, near Port Angeles, Washington	12045500	Ca	13.44	58	$Ca = 12.4 + 2.6 \left(\frac{1}{1 + 10^{-3.8Q}} \right)$.03	25.9
		Mg	1.28	58	$Mg = 1.33 - 71.83(1/Q)$.00	2.5
		Na	2.02	58	$Na = 1.17 + 1.25 \left(\frac{1}{1 + 3.16 \times 10^{-4}Q} \right)$.10	3.9
		K	0.21	58	$K = 0.234 - 33.97(1/Q)$.02	0.4
		SO ₄	8.03	58	$SO_4 = 4.0 + 5.95 \left(\frac{1}{1 + 3.16 \times 10^{-4}Q} \right)$.10	15.5
		Cl	1.06	58	$Cl = 0.853 + 3.24 \left(\frac{1}{1 + 10^{-3.8Q}} \right)$.07	2.04
		SiO ₂	5.60	82	nc	nc	10.8
		mean ^a pH	7.6	26	nc	nc	nc
Dungeness River near Sequim, Washington	12018600	Ca	15.56	27	$Ca = 12.2 + 36.95(1/Q)$.64	13.4
		Mg	2.19	27	$Mg = 1.71 + 5.32(1/Q)$.35	1.9
		Na	2.63	27	$Na = 1.90 + 8.00(1/Q)$.53	2.3
		K	0.38	27	nc	nc	0.3
		SO ₄	6.93	21	$SO_4 = 5.32 + 17.7(1/Q)$.62	6.0
		Cl	1.03	26	$Cl = 0.44 + 6.53(1/Q)$.42	0.9
		SiO ₂	5.95	14	$LN(SiO_2) = 2.16 - 0.157LN(Q)$.34	5.1
		median pH	7.7	27	nc	nc	nc
Nooksack River at Deming, Washington	12210500	Ca	9.26	37	$LN(Ca) = 2.44 - 0.0026(Q)$.69	18.3
		Mg	2.63	37	$LN(Mg) = 1.77 - 0.183LN(Q)$.29	5.1
		Na	1.62	37	$LN(Na) = 1.64 - 0.254LN(Q)$.47	3.2
		K	0.53	42	nc	nc	1.0
		SO ₄	7.96	36	$LN(SO_4) = 3.73 - 0.364LN(Q)$.59	15.7
		Cl	0.88	41	nc	nc	1.7
		SiO ₂	7.09	18	$LN(SiO_2) = 2.12 - 0.00170(Q)$.49	14.0
		mean pH	7.3	50	nc	nc	nc
Baker River at Concrete, Washington	12193500	Cl/Na	nc	42	$Na = 1.27 + 0.41(Cl)$.19	nc
		SO ₄ /Ca	nc	41	$LN(Ca) = 1.15 + 0.487LN(SO_4)$.48	nc
		Ca	6.78	64	nc	nc	20.9
		Mg	1.05	64	nc	nc	3.2
		Na	1.41	64	nc	nc	4.3
		K	0.51	64	nc	nc	1.5
		SO ₄	7.91	64	nc	nc	24.4
		Cl	0.72	64	nc	nc	2.2
Skagit River near Mount Vernon	12200500	SiO ₂	6.79	16	nc	nc	21.0
		mean ^a pH	7.0	20	nc	nc	nc
		Ca	6.78	126	$LN(Ca) = 2.1 - 0.00039(Q)$.20	12.6
		Mg	1.31	127	nc	nc	2.44
		Na	1.32	127	$LN(Na) = 0.535 - 0.00055(Q)$.29	2.46
		K	0.57	127	nc	nc	1.06
		SO ₄	4.68	125	nc	nc	8.70
		Cl	0.78	127	nc	nc	1.45
Samish River near Burlington, Washington	12201500	SiO ₂	6.26	126	$LN(SiO_2) = 2.01 - 0.00037(Q)$.25	11.7
		mean ^a pH	7.2	120	nc	nc	nc
		Ca	6.91	44	$LN(Ca) = 2.37 - 0.227LN(Q)$.90	6.6
		Mg	2.03	44	$Mg = 1.75 + 1.94(1/Q)$.85	1.9
		Na	2.82	44	$Na = 2.69 + 0.89(1/Q)$.53	2.7
		K	0.66	44	$K = 0.617 + 0.288(1/Q)$.19	0.6
		SO ₄	5.00	44	nc	nc	4.8
		Cl	2.51	44	nc	nc	2.4
		SiO ₂	6.66	44	$SiO_2 = 5.99 + 4.59(1/Q)$.79	6.4
		mean ^a pH	7.1	48	nc	nc	nc
		Cl/Na	nc	44	nc	nc	nc
		SO ₄ /Ca	nc	44	nc	nc	nc

Appendix B.--Average concentration-continued.

Name	Number	Dissolved constituent	Concentration at mean annual discharge, in mg/L	N	Regression equation	R ²	Annual gross loss, in T/km ²
North Fork Stillaguamish River near Arlington	12167000	Ca	5.45	27	LN(Ca)=3.03-0.335LN(Q)	.83	13.6
		Mg	1.48	27	Mg=1.21+14.69(1/Q)	.69	3.7
		Na	1.52	27	LN(Na)=1.80-0.347LN(Q)	.84	3.8
		K	0.40	27	K=0.31+4.80(1/Q)	.62	1.0
		SO ₄	2.57	27	LN(SO ₄)=1.49-0.137LN(Q)	.28	6.4
		Cl	0.96	27	Cl=0.694+14.46(1/Q)	.54	2.4
		SiO ₂	5.88	27	SiO ₂ =5.09+42.47(1/Q)	.64	14.7
		mean ^a pH	7.2	24	nc	nc	nc
		Cl/Na	nc	27	Na=0.81+0.77(Cl)	.70	nc
		SO ₄ /Ca	nc	27	Ca=0.38+2.40(SO ₄)	.48	nc
Skykomish River near Gold Bar, Washington	12134500	Ca	3.69	45	LN(Ca)=2.25-0.20LN(Q)	.55	9.4
		Mg	0.54	45	Mg=0.45+9.71(1/Q)	.15	1.4
		Na	1.49	45	LN(Na)=1.84-0.305LN(Q)	.67	3.8
		K	0.48	45	LN(K)=0.556-0.0015(Q)	.26	1.2
		SO ₄	2.08	43	nc	nc	5.3
		Cl	0.97	45	Cl=0.592+42.7(1/Q)	.59	2.5
		SiO ₂	5.31	26	LN(SiO ₂)=1.78+0.00098(Q)	.32	13.5
		mean ^a pH	7.1	40	nc	nc	nc
		Cl/Na	nc	45	Na=0.878+0.63(Cl)	.49	nc
		SO ₄ /Ca	nc	43	Ca=2.99+0.41(SO ₄)	.23	nc
Issaquah Creek near Issaquah, Washington	12121600	Ca	8.51	69	LN(Ca)=2.53-0.264LN(Q)	.93	8.2
		Mg	3.01	69	LN(Mg)=1.53-0.294LN(Q)	.88	2.9
		Na	4.69	69	LN(Na)=1.92-0.257LN(Q)	.90	4.5
		K	0.69	68	K=0.55+0.619(1/Q)	.57	0.7
		SO ₄	6.39	69	LN(SO ₄)=2.07-0.146LN(Q)	.52	6.1
		Cl	2.43	68	LN(Cl)=1.06-0.119LN(Q)	.30	2.3
		SiO ₂	14.7	45	LN(SiO ₂)=2.92-0.159LN(Q)	.82	14.1
		mean ^a pH	7.0	36	nc	nc	nc
		Cl/Na	nc	68	Na=1.29+1.53(Cl)	.34	nc
		SO ₄ /Ca	nc	69	Ca=1.70+1.14(SO ₄)	.50	nc
Cedar River at Renton, Washington	12119000	Ca	7.09	38	LN(Ca)=2.64-0.229LN(Q)	.86	9.0
		Mg	1.45	38	LN(Mg)=1.31-0.313LN(Q)	.76	1.8
		Na	2.59	38	LN(Na)=1.68-0.244LN(Q)	.89	3.3
		K	0.43	38	LN(K)=0.057-0.302LN(Q)	.46	0.5
		SO ₄	3.16	38	SO ₄ =5.24-0.698LN(Q)	.48	4.0
		Cl	1.17	37	LN(Cl)=0.740-0.196LN(Q)	.45	1.5
		SiO ₂	10.47	38	LN(SiO ₂)=2.77-0.141LN(Q)	.72	13.2
		mean ^a pH	7.3	52	nc	nc	nc
		Cl/Na	nc	37	Na=0.726+1.69(Cl)	.58	nc
		SO ₄ /Ca	nc	38	Ca=2.98+1.44(SO ₄)	.52	nc
Green River near Kent, Washington	12113340	Ca	7.59	65	LN(Ca)=3.20-0.313LN(Q)	.70	9.1
		Mg	1.87	64	Mg=1.47+17.02(1/Q)	.62	2.2
		Na	4.57	65	LN(Na)=3.01-0.40LN(Q)	.78	5.4
		K	0.89	64	K=0.80+3.8(1/Q)	.11	1.1
		SO ₄	4.20	64	SO ₄ =3.87+13.79(1/Q)	.10	5.0
		Cl	3.11	65	Cl=1.56+65.88(1/Q)	.67	3.7
		SiO ₂	14.0	nc	nc	nc	16.7
		mean ^a pH	7.2	60	nc	nc	nc
		Cl/Na	nc	65	Na=1.93+0.803(Cl)	.91	nc
		SO ₄ /Ca	nc	64	Ca=3.81+1.06(SO ₄)	.29	nc
Big Soos Creek near Auburn, Washington	12112610	Ca	9.46	98	LN(Ca)=2.35-0.0284(Q)	.69	6.2
		Mg	3.44	98	LN(Mg)=1.37-0.105(LN(Q)	.58	2.3
		Na	5.34	98	nc	nc	3.5
		K	1.03	97	nc	nc	0.7
		SO ₄	8.55	98	LN(SO ₄)=1.95+0.152LN(Q)	.41	5.6
		Cl	2.64	98	nc	nc	1.7
		SiO ₂	13.51	58	LN(SiO ₂)=2.83-0.175LN(Q)	.67	8.9
		mean ^a pH	7.3	60	nc	nc	nc
		Cl/Na	nc	98	nc	nc	nc
		SO ₄ /Ca	nc	98	Ca=12.0-0.030(SO ₄)	nc	nc

Appendix B.--Average concentration-continued.

Name	Number	Dissolved constituent	Concentration at mean annual discharge, in mg/L	N	Regression equation	R ²	Annual gross loss, in T/km ²
Puyallup River at Puyallup, Washington	12101500	Ca	6.59	193	$LN(Ca)=2.76-0.192LN(Q)$.31	8.1
		Mg	1.67	193	$LN(Mg)=1.68-0.256LN(Q)$.26	2.0
		Na	3.52	193	$LN(Na)=2.26-0.22LN(Q)$.42	4.3
		K	0.82	193	$K=1/(-14.90(1/Q)+1.38)$.08	1.0
		SO ₄	6.25	191	$LN(SO_4)=3.2-0.30LN(Q)$.32	7.7
		Cl	1.86	193	$Cl=1.28+55.46(1/Q)$.25	2.3
		SiO ₂	13.87	82	$SiO_2=13.14+69.76(1/Q)$.05	17.1
		median pH	7.2	183	nc	nc	nc
		Cl/Na	nc	193	$Na=2.54+0.53(Cl)$.32	nc
		SO ₄ /Ca	nc	190	$Ca=4.52+0.34(SO_4)$.24	nc
Nisqually River at McKenna, Washington	12089500	Ca	5.24	43	$Ca=5.19+3.16(1/Q)$.55	7.9
		Mg	1.37	43	$Mg=1.35+1.46(1/Q)$.47	2.0
		Na	3.13	43	$Na=3.11+1.28(1/Q)$.35	4.7
		K	0.63	43	nc	nc	0.9
		SO ₄	2.26	43	nc	nc	3.4
		Cl	1.67	43	nc	nc	2.5
		SiO ₂	14.6	43	$SiO_2=13.62+5.05(1/Q)$.10	21.3
		mean pH	7.2	45	nc	nc	nc
		Cl/Na	nc	43	$Na=2.69+0.32(Cl)$.17	nc
		SO ₄ /Ca	nc	43	$Ca=4.19+0.56(SO_4)$.28	nc
Cowlitz River near Randle, Washington	14233400	Ca	5.74	57	$LN(Ca)=3.09-0.269LN(Q)$.50	9.8
		Mg	0.97	58	$Mg=0.80+24.7(1/Q)$.33	1.7
		Na	2.75	58	$LN(Na)=2.11-0.224LN(Q)$.48	4.7
		K	0.48	58	$K=0.37+15.63(1/Q)$.25	0.8
		SO ₄	1.82	57	$SO_4=6.74-0.987LN(Q)$.69	3.1
		Cl	0.99	58	$LN(Cl)=2.26-0.455LN(Q)$.35	1.7
		SiO ₂	12.64	36	$LN(SiO_2)=2.78-0.00166(Q)$.49	21.6
		mean pH	7.3	48	nc	nc	nc
		Cl/Na	nc	58	$LN(Na)=1.03+0.27LN(Cl)$.41	nc
		SO ₄ /Ca	nc	56	$LN(Ca)=1.55-0.41LN(SO_4)$.42	nc
Toutle River near Castle Rock, Washington	14242700	Ca	3.83	46	$LN(Ca)=2.35-0.24LN(Q)$.63	5.8
		Mg	0.98	48	$Mg=0.78+12.62(1/Q)$.48	1.5
		Na	3.62	48	$LN(Na)=2.69-0.339LN(Q)$.91	5.5
		K	0.72	48	nc	nc	1.1
		SO ₄	2.76	48	nc	nc	4.1
		Cl	3.09	48	nc	nc	4.6
		SiO ₂	15.0	nc	nc	nc	22.0
		median pH	nc	48	nc	nc	nc
		Cl/Na	nc	48	$Na=0.60+1.13(Cl)$.74	nc
		SO ₄ /Ca	nc	46	nc	nc	nc
Lewis River at Ariel, Washington	14220500	Ca	3.89	68	nc	nc	8.9
		Mg	0.90	68	nc	nc	2.1
		Na	2.64	68	nc	nc	6.1
		K	0.45	68	nc	nc	1.0
		SO ₄	2.27	68	nc	nc	5.2
		Cl	1.60	68	nc	nc	3.7
		SiO ₂	14.3	19	nc	nc	32.8
		median pH	7.1	54	nc	nc	nc

nc = not calculated

a/ Leibbrand (1970)